Phase Transition Kinetics in Langmuir and Spin-Coated Polydiacetylene Films

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1. AFM images of SC PDA films

Figure S1: AFM images of SC PDA film (a) before and (b) during the degradation stage; (c) Section analysis along the black line shown in (a). Note the good coverage of the PDA film in (a) with the well-defined step from the film to the quartz substrate while image (b) depicts fragments remaining from the degraded film.
2. The kinetic model

2.1 Simple Kinetic Model

M – Monomer phase (the unpolymerized part of the film)
P – Polymer phase (the polymerized part of the film)
D – Degradation phase (the part of the film that was damaged and eventually removed from the substrate)

Two exposure-dependent kinetic constants, $k_1$ and $k_5$ (Wscm$^{-2}$)$^{-1}$, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by Formula (1):

\[
M \xrightarrow{k_1} P \xrightarrow{k_5} D
\]

The M→P transition is described by $k_1$ and the P→D transitions are described by $k_5$.

Setting the initial amount of monomer to unity, the fractions of the monomer M, polymer P and degradation stage D as a function of radiation exposure, $H$, (Wscm$^{-2}$) can be calculated using Equations (2)-(4):

\[
\frac{dM}{dH} = -k_1 M \rightarrow M = M e^{-k_1H}
\]

\[
\frac{dP}{dH} = k_1 M - k_5 P \rightarrow P = \frac{k_1}{k_5 - k_1} (e^{-k_1H} - e^{-k_5H})
\]

\[
\frac{dD}{dH} = k_5 P \rightarrow D = 1 + \frac{k_1 e^{-k_1H} - k_5 e^{-k_5H}}{k_5 - k_1}
\]

2.2 Unidirectional Kinetic Model

The following phases are present:

M – Monomer phase (the unpolymerized part of the film with starting amount of $M_0$)
B – Blue phase (the polymerized part of the film in the blue phase)
R – Red phase (the polymerized part of the film in the red phase)
D – Degradation phase (the part of the film that was damaged)

Three exposure–reciprocal kinetic constants, $k_1$, $k_2$ and $k_6$ (Wscm$^{-2}$)$^{-1}$, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by:

\[
M \xrightarrow{k_1} B \xrightarrow{k_2} R \xrightarrow{k_6} D
\]

The phases evolve with flux $H$ of UV radiation according to:

\[
\frac{dM}{dH} = -k_1 M
\]

\[
\frac{dB}{dH} = k_1 M - k_2 B - k_6 B
\]

\[
\frac{dR}{dH} = k_2 B - k_6 R
\]

\[
\frac{dD}{dH} = k_6 R + k_6 B = k_6 (B + R)
\]

The solution for $M$ is

\[
M = e^{-k_1H}
\]
with all quantities in units of the starting monomer M₀ proceed by considering the sum B+R so that

\[
\frac{dP}{dH} = \frac{d(B+R)}{dH} = k_1M - (B+R)k_2
\]

\[
B + R = \frac{k_1}{k_3} (e^{\lambda_H} - e^{-\lambda_H})
\]

To solve D to place Eq. (12) into Eq. (9)

\[
\frac{dD}{dH} = k_1R + k_2B = k_1(R+B) = k_1\left[ \frac{k_1}{k_3 - k_1}(e^{\lambda_H} - e^{-\lambda_H}) \right]
\]

\[
D = 1 + \frac{k_1 e^{\lambda_H} - e^{-\lambda_H}}{k_3 - k_1}
\]

For B we plot:

\[
\frac{dB}{dH} = k_1M - k_1B - k_2B = k_1M - B(k_2 + k_3)
\]

\[
B = \frac{k_1}{(k_2 + k_3 - k_1)} (e^{\lambda_H} - e^{-\lambda_H})
\]

And finally to solve R:

\[
\frac{dR}{dH} = k_1B - k_2R
\]

\[
R = k_1(k_1 e^{\lambda_H} - (k_2 + k_3 - k_1)e^{-\lambda_H} + (k_3 - k_1)e^{-(k_2 + k_3)H})
\]

\[
(k_2 + k_3 - k_1)(k_3 - k_1)
\]

2.3 Reversible Kinetic Model

The following phases are present:

**M** – Monomer phase (the unpolymerized part of the film with starting amount of M₀)

**B** – Blue phase (the polymerized part of the film in the blue phase)

**I** – Intermediate phase (intermediate phase in the blue to red transition)

**R** – Red phase (the polymerized part of the film in the red phase)

**D** – Degradation phase (the part of the film that was damaged)

Five exposure–reciprocal kinetic constants, k₁-k₅ (Wscm⁻²)⁻¹, were defined in order to describe the transformation rate in each stage of the reaction as a function of UV dose. The phase transitions of PDA are schematically presented by:

\[
M \xrightarrow{k_1} B \xrightarrow{k_3} I \xrightarrow{k_2} R \xrightarrow{k_5} D
\]

We derive here the solution for the kinetic equations, including the putative new phase I. The M equation is solved by \( M = e^{\lambda_H} \) (normalizing the initial monomer to unity), hence the B and I equations can be written in a matrix form as

\[
\frac{d}{dH} \begin{pmatrix} B \\ I \end{pmatrix} = \begin{pmatrix} k_1 e^\lambda_H & 0 \\ 0 & -k_3 \end{pmatrix} \begin{pmatrix} B \\ I \end{pmatrix}
\]
where
\[
\hat{F} = \begin{pmatrix}
  (k_2 + k_3) & -k_1 \\
  -k_2 & (k_2 + k_4 + k_5)
\end{pmatrix} = a_i \hat{I} + a_i \hat{\sigma}_x + a_i \hat{\sigma}_y + a_i \hat{\sigma}_z,
\]
where \(\hat{\sigma}_x\), \(\hat{\sigma}_y\), and \(\hat{\sigma}_z\) are standard Pauli matrices and \(\hat{I}\) is a unit matrix. The coefficients are:

(22) \(a_i = \frac{1}{2}(k_2 + k_4 + 2k_5 + k_3)\)

(23) \(a_i = -\frac{1}{2}(k_2 + k_3)\)

(24) \(a_i = \frac{1}{2}(k_2 - k_3)\)

(25) \(a_i = \frac{1}{2}(k_2 - k_1 - k_3)\)

We rewrite the matrix in terms of a unit vector \(\vec{n}\) and a vector \(\vec{\sigma}\) of the Pauli matrices:

(26) \(\hat{F} = a_i \hat{I} + a_i \vec{\sigma} \cdot \vec{n}\)

(27) \(\vec{n} = \frac{1}{2}(a_i, ia_i, a_i)\)

(28) \(\alpha = \frac{\sqrt{a_i^2 + a_i^2 - a_2^2}}{2} = \frac{1}{2} \sqrt{4k_2k_3 + (k_2 - k_3)^2} > 0\)

Using identities of Pauli matrices we have:

(29) \(e^{i\alpha \hat{B} \cdot \vec{n} - \alpha \hat{H} \hat{\sigma}} = \cosh \left(\alpha H\right) \hat{I} + \sinh \left(\alpha H\right) \vec{\sigma} \cdot \vec{n}\)

The kinetic equation can be written in terms of:

(30) \(\begin{pmatrix} B \\ I \end{pmatrix} = e^{-\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \begin{pmatrix} B \\ I \end{pmatrix}\)

so that

(31) \(\frac{d}{d\alpha} \begin{pmatrix} B \\ I \end{pmatrix} = e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \begin{pmatrix} k_\hat{e}^{-\alpha H} \\ 0 \end{pmatrix}\)

Using the identity above for the exponent we get:

(32) \(e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} = e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \begin{pmatrix} \cosh \left(\alpha H\right) \hat{I} + \sinh \left(\alpha H\right) \left(\hat{F} - a_i \hat{I}\right) \frac{1}{\alpha} \end{pmatrix}\)

(33) \(e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \begin{pmatrix} k_\hat{e}^{-\alpha H} \\ 0 \end{pmatrix} = \left[e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \cosh \left(\alpha H\right) \hat{I} + e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \sinh \left(\alpha H\right) \frac{1}{\alpha} \left(\frac{a_i}{a_i - a_1} \frac{a_i + a_2}{-a_3} \right) \right] \begin{pmatrix} k_\hat{e}^{-\alpha H} \\ 0 \end{pmatrix}\)

Hence the kinetic equation becomes:

(34) \(\frac{d}{d\alpha} \begin{pmatrix} B \\ I \end{pmatrix} = \left[ e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \cosh \left(\alpha H\right) \hat{I} + e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \sinh \left(\alpha H\right) a_i \hat{e}^{-\alpha H} \right] \begin{pmatrix} B \\ I \end{pmatrix} \)

After a straightforward integration and transforming back to B and N variables we obtain

(35) \(\begin{pmatrix} B \\ I \end{pmatrix} = e^{-\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \begin{pmatrix} B \\ I \end{pmatrix} = e^{-\alpha \hat{B} \cdot \vec{n}} \left[ \cosh \left(\alpha H\right) \hat{I} - \frac{\sinh \left(\alpha H\right)}{\alpha} \left(\frac{a_i}{a_i - a_2} \frac{a_i + a_2}{-a_3} \right) \right] \begin{pmatrix} B \\ I \end{pmatrix}\)

so that finally

(36) \(B = \frac{1}{2} k_2 \left[ e^{\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \frac{1 + a_2}{a_i - a_2} + e^{-\frac{1}{\alpha} \hat{H} \cdot \vec{n}} \frac{1 - a_2}{a_i - a_2} \right] \)
The kinetic equations for the polymer content $P=B+I+R$ are identical to those of the model Eq. (1) so that we can use the solution for $P$ and $D$ of that model, and for the red phase:

$$R = P - B - I$$